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Exact Exchange-Correlation Treatment of Dissociated H_2 in Density Functional Theory

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Whereas the wave function of the dissociated H_2 molecule is easily obtained, an exact treatment of this system has not yet been given in density functional theory. We propose an orbital dependent exchange-correlation functional that yields this exact Kohn-Sham solution. This type of functional offers an alternative to local-density and generalized gradient approximations and the prospects are indicated for treating with it some outstanding problems in density functional theory.

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The dissociation of H_2, as a prototype for dissociation of electron pair bonds in general, is an important problem in electronic structure theory. Simple wave functions for this case, such as the Heitler-London wave function and the molecular orbital wave function, have in the early days of quantum mechanics strongly influenced our way of thinking about the quantum mechanical description of chemical bonding. In density functional theory (DFT) [1,2] the dissociation of H_2 is still an unsolved problem. However, an exact solution of this prototype system is possible in DFT, as we will show, and the solution points the way to further development, as it did for the other major electronic structure approaches to chemical bonding.

The MO wave function $\Psi^{\mathrm{MO}} = |\sigma_g \overline{\sigma}_g|$ has much too high an energy at $R \rightarrow \infty$ due to the 50% contribution of high energy ionic determinants $|a\overline{a}|$ and $|b\overline{b}|$ (a and b are the $1s$ atomic orbitals on nucleus A and B, respectively). When the σ_g orbital is optimized in a Hartree-Fock (HF) calculation it does not become a linear combination of the $1s$ orbitals, but the wave function and electron density become much too diffuse in an attempt to minimize the energy penalty of the ionic determinants. This failure of HF can also be described in terms of the potential in which the electrons move. In Fig. 1 the Fermi hole and the Coulomb hole that surround a reference electron are plotted. The Fermi hole, containing -1 electron, is $-(1/2)\rho$ irrespective of the position of the reference electron and removes only $1/2$ electron at both sides. The HF potential thus leaves, when the electron is close to nucleus B say, an electron density $|b|^2/2$ around this nucleus which partly screens it and causes the HF σ_g orbital [as well as the similar exact-exchange Kohn-Sham (KS) orbital] to become (much) too diffuse. In order that a one-electron effective potential such as the Kohn-Sham potential builds the correct density, it needs to incorporate the correlation hole (or Coulomb hole) potential v_c^{hole}, so that the total hole for an electron close to B becomes $-|b|^2$ and the electron sees the nucleus unscreened; see Fig. 1. The Coulomb hole potential is included in the exact Kohn-Sham potential [3,4].

Local-density (LDA) and generalized gradient (GGA) approximation calculations on dissociating H_2 also fail. The problem basically is that the charge density around each nucleus is identical in this system to that in a free H atom. It is virtually impossible to devise functionals that use only local information (local density and derivatives of the density) and still recognize the position of the other H atom and build correctly the delocalized Fermi and Coulomb holes whose shapes are determined by the positions of the nuclei (see Fig. 1 for H_2; for other molecules, see Refs. [5,6]). The exchange and correlation energies are very different from those in two isolated H atoms, for instance, the correlation energy density is zero in H atom but substantial around each H atom in H_2 at long distance [7]. Table I shows the GGA works quite well both for exchange and correlation at R_e, but at $R = 5.0$ bohr the errors in the exchange and correlation energies become individually large (on the order of 3 eV) and only partly compensate each other.

Spin and symmetry unrestricted calculations can yield good energies upon dissociation [8,9] but do not yield a proper symmetry adapted solution. In fact, all along the dissociation coordinate of H_2 the proper symmetrical KS potential and the corresponding determinant with a doubly occupied σ_g orbital describing the exact density exist [10]. At $R \rightarrow \infty$ the potential has the required $-1/r_a$ and $-1/r_b$ shape around the nuclei. In this paper we wish to demonstrate that this potential, and an exact total energy, can be derived from a simple ansatz for the exchange-correlation

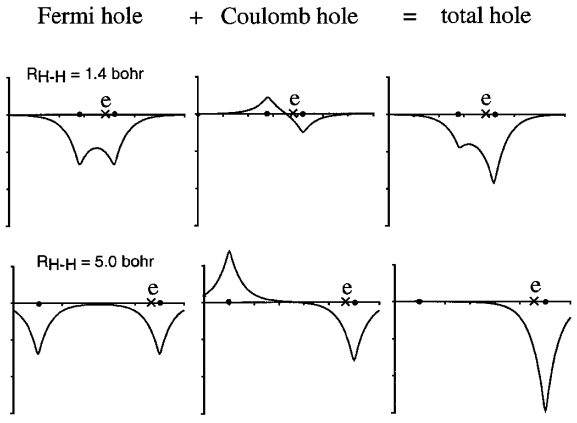

FIG. 1. Fermi hole [$= -(1/2)\rho$], Coulomb hole, and total hole in the hydrogen molecule at $R = 1.4$ (equilibrium distance) and 5.0 bohr. The reference electron is always placed at 0.3 bohr to the left of the right H atom.

TABLE I. Contributions (in eV) to the exchange and correlation energies in H_2 at the equilibrium distance $R = 1.401$ bohr, and at long distance. The exact-exchange energy is compared to a GGA exchange energy consisting of the LDA part plus the Becke correction. The exact correlation contribution to the two-electron energy W is compared to the Perdew-Wang approximation.

R (bohr)	E_x^{LDA}	$\Delta E_x^{\mathrm{Becke}}$	E_x^{GGA}	E_x^{exact}	W_c^{PW}	W_c^{exact}
1.401	−15.48	−2.42	−17.90	−17.99	−2.20	−1.93
5.0	−11.51	−2.42	−13.93	−11.16	−1.55	−5.63

functional E_{xc}. We take as our point of departure the expression of the Fermi hole as the square of a hole amplitude by Luken *et al.* [11,12]:

$$E_x = -\frac{1}{4}\int \frac{|\gamma(r_1,r_2)|^2}{r_{12}}\,dr_1\,dr_2 = \frac{1}{2}\int \rho(r_1)\nu_x^{\mathrm{hole}}(r_1)\,dr_1 = \frac{1}{2}\int dr_1\,\rho(r_1)\int dr_2\,\frac{-|\varphi^{\mathrm{Fermi}}(r_2\,|\,r_1)|^2}{r_{12}} \quad (1)$$

(since we are dealing with a closed shell system, we use for brevity of notation spin-integrated quantities throughout). The amplitude $\varphi^{\mathrm{Fermi}}(r_2\,|\,r_1)$ describing a hole around the reference position r_1 can be written as $\varphi^{\mathrm{Fermi}}(r_2\,|\,r_1) = \sum_{i=1}^{N/2}[\sqrt{f_i}\,\varphi_i^*(r_1)/\sqrt{\rho(r_1)}]\varphi_i(r_2)$. So the hole amplitude around r_1 is expanded in the occupied orbitals (f_i refers to the HF occupation number) with coefficients that depend on the reference position. Much of the shape and behavior of Fermi holes can be understood from this expression [5,12]. It has been demonstrated [6,13] that this Fermi hole amplitude can be generalized in very good approximation to a full exchange-correlation hole amplitude by including both strongly and weakly occupied natural orbitals (NO's): $\varphi^{\mathrm{hole}}(r_2\,|\,r_1) = \sum_i[w_i\varphi_i^*(r_1)/\sqrt{\rho(r_1)}]\varphi_i(r_2)$. Here the weights w_i are equal to $\sqrt{n_i}$, where the n_i are the NO occupation numbers, and the φ_i are the NO's. This hole expression may be derived from general conditions on the two-electron density matrix, as proper permutation symmetry between the electron coordinates, and integration of the two-electron density matrix to $N-1$ times the one-matrix [6,13]. This expression describes correlation remarkably well for cases of dynamical correlation, such as He [becoming exact in the high Z two-electron ions with configuration $(1s)^2$] and also for cases of near degeneracy or nondynamical correlation. When expressing a hole amplitude in terms of KS orbitals we are led to invoke both occupied and unoccupied KS orbitals with weights that cannot be derived from their KS occupations f_i (we use f_i for both HF and KS occupation numbers, they are all 2 or 0 for closed shell systems). In a case such as H_2 at $R \to \infty$, where the σ_g and σ_u KS orbitals and NO's are actually identical [given by $(a \pm b)/\sqrt{2}$], we can take the KS orbital weight equal to the $\sqrt{n_i}$, i.e., the weights of the KS orbitals in the hole amplitude are 1 for both σ_g and σ_u. It is easily seen that our hole amplitude φ^{hole} correctly yields a hole of shape $-|a|^2$ when r_1 is in the neighborhood of atom A, $r_1 \in \Omega_A$, and the hole is $-|b|^2$ when $r_1 \in \Omega_B$. The expression for E_{xc} becomes (φ_1 and φ_2 are σ_g and σ_u, respectively)

$$E_{\mathrm{xc}} = \frac{1}{2}\int dr_1\,\rho(r_1)\int dr_2\,\frac{-|\varphi^{\mathrm{hole}}(r_2\,|\,r_1)|^2}{r_{12}} = -\frac{1}{2}\sum_{i,j=1}^{2}\int dr_1\,dr_2\,\varphi_i^*(r_1)\varphi_i(r_2) \times \varphi_j(r_1)\varphi_j^*(r_2)/r_{12}\,. \quad (2)$$

This expression for E_{xc} yields the exact total energy at $R \to \infty$ provided that the KS potential corresponding to this E_{xc} is correct, i.e., provided ν_{xc} is the potential of a proper hole that corrects for the screening of the nuclear potentials by the total electron density present in the Hartree potential. In that case the orbital shapes around A and B will be exact, and the kinetic energy and the electron-nuclear energy are then exact. The xc potential can be called exact in the sense that it delivers the exact energy and KS potential (we are neglecting the van der Waals energy). Of course, the energy density, for which we use the potential of the exchange-correlation hole density, is not a unique spatial function. The λ coupling constant integration is often invoked to provide an alternative xc energy density, namely, the potential of an effective hole density that incorporates the energy density for the correlation contribution to the kinetic energy, T_c. We note however that in H_2 at $R \to \infty$ $T_c = 0$ and the λ integration has no effect [14]. E_{xc} of Eq. (2) is a manifestly nonlocal functional of ρ, i.e., the energy density at a point is not obtained from the density and its derivatives at that point. We strictly adhere, however, to the Kohn-Sham model for the noninteracting auxiliary electron system, with a local potential and an *Aufbau* orbital occupation. We proceed to demonstrate that the local KS potential that can be derived from E_{xc} [Eq. (2)] is correct, so that φ_1 and φ_2 are the correct σ_g and σ_u orbitals and our ansatz for φ^{hole} yields a consistent solution for the dissociated H_2 system.

Since the KS orbitals are themselves functionals of the density we can write

$$\nu_{\mathrm{xc}}(r) = \frac{\delta E_{\mathrm{xc}}[\{\varphi_i[\rho]\}]}{\delta\rho(r)} = \sum_i\int \frac{\delta E_{\mathrm{xc}}}{\delta\varphi_i(r')}\frac{\delta\varphi_i(r')}{\delta\nu_s(r'')}\frac{\delta\nu_s(r'')}{\delta\rho(r)}\,dr'\,dr'' + \text{c.c.} = -\sum_i\int \frac{\delta E_{\mathrm{xc}}}{\delta\varphi_i(r')}\,G_i(r',r'')\varphi_i(r'')\chi_s^{-1}(r'',r)\,dr'\,dr'' + \text{c.c.}\,, \quad (3)$$

where we have used the orbital Green's function $G_i(r',r'') = \sum_{j\neq i}\varphi_j(r')\varphi_j^*(r'')/(\varepsilon_j - \varepsilon_i)$ which describes the response

of an orbital to a change of potential $\delta\nu_s$: $\delta\varphi_i(r') = -\int G_i(r', r'')\varphi_i(r'')\delta\nu_s(r'')\,dr''$. The constraint that the KS orbitals be solutions in a local KS potential $\nu_s(r)$ is explicitly applied in the optimized potential method [15], but is here introduced by the use of the chain rule in the functional derivation in Eq. (3). Multiplying by the density response function $\chi_s(r, r_1) = -\sum_{i=1}^{N/2} f_i\varphi_i^*(r)G_i(r, r_1)\varphi_i(r_1) + \text{c.c.}$ and integrating over r we obtain an integral equation for ν_{xc}:

$$\int \nu_{\text{xc}}(r)\chi_s(r, r_1)\,dr = \sum_i \int \nu_i(r')\varphi_i^*(r')G_i(r', r_1) \times \varphi_i(r_1)\,dr' + \text{c.c.} \tag{4}$$

We have introduced the potentials $\nu_i(r') = [1/\varphi_i^*(r')]\delta E_{\text{xc}}/\delta\varphi_i(r')$ for comparison to developments in optimized potential methods [15,16], but note that we do not divide by any occupation number. The summation over i at the right-hand side runs over occupied as well as unoccupied KS orbitals. If for E_{xc} one uses the exchange-only functional E_x, the summation runs over occupied orbitals only and the exact-exchange KS potential simplifies in our case of one doubly occupied orbital to just one term, i.e., $\nu_x^{\text{EXX}}(r_1) = (1/2)\nu_1^{\text{EXX}}(r_1) = -(1/2)\int 2|\varphi_1(r_2)|^2/r_{12}\,dr_2$, i.e., just the Fermi hole potential. With our E_{xc} both ν_1 and ν_2 (and ν_1^* and ν_2^*) play a role:

$$\begin{aligned}\nu_1(r_1) &= -\int \frac{|\varphi_1(r_2)|^2}{r_{12}}\,dr_2 - \frac{\varphi_2^*(r_1)}{\varphi_1^*(r_1)}\int \frac{\varphi_1^*(r_2)\varphi_2(r_2)}{r_{12}}\,dr_2\,,\\ \nu_2(r_1) &= -\int \frac{|\varphi_2(r_2)|^2}{r_{12}}\,dr_2 - \frac{\varphi_1^*(r_1)}{\varphi_2^*(r_1)}\int \frac{\varphi_1(r_2)\varphi_2^*(r_2)}{r_{12}}\,dr_2\end{aligned} \tag{5}$$

(since we are dealing with a closed shell system with real orbitals, we henceforth simplify to real orbitals). Note that the first term in ν_1 lacks the factor 2 present in ν_1^{EXX}, which is a consequence of the different weight of φ_1 in E_{xc} than in E_x ("occupation" 1 rather than 2). The second term of ν_1 causes localization of the hole. When the reference position r_1 is in the neighborhood of nucleus A, $r_1 \in \Omega_A$, the factor $\varphi_2(r_1)/\varphi_1(r_1) = 1$ and ν_1 is the potential of the hole charge $-(|\varphi_1|^2 + \varphi_1\varphi_2) = -|a|^2 + ab$. For $r_1 \in \Omega_B$, the hole for $\nu_1(r_1)$ is $-|b|^2 + ab$. So the potential ν_1 associated with the occupied orbital $\varphi_1 = \sigma_g$ now has proper local behavior. Also ν_2 can easily be checked to arise from the local holes $-|a|^2 - ab$ and $-|b|^2 - ab$, respectively.

In order to exhibit the way in which ν_1 and ν_2 enter into ν_{xc} we solve for ν_{xc} analytically, using the approach followed in the exchange-only case by Krieger *et al.* [15] (cf. also [17]). Introducing for our system the small difference $\delta = \varepsilon_2 - \varepsilon_1$ and the large difference $\Delta = \varepsilon_j - \varepsilon_1$ for all $j > 2$, we can approximate G_1 and G_2 as

$$\begin{aligned}G_1(r_1, r_2) &= \frac{1}{\Delta}\left[\delta(r_1 - r_2) - \varphi_1(r_1)\varphi_1(r_2) + \frac{\Delta - \delta}{\delta}\,\varphi_2(r_1)\varphi_2(r_2)\right],\\ G_2(r_1, r_2) &= \frac{1}{\Delta}\left[\delta(r_1 - r_2) - \varphi_2(r_1)\varphi_2(r_2) - \frac{\Delta + \delta}{\delta}\,\varphi_1(r_1)\varphi_1(r_2)\right].\end{aligned} \tag{6}$$

Defining $\overline{\nu}(r) = \nu_1(r)\,|\varphi_1(r)|^2/\rho(r) + \nu_2(r)\,|\varphi_2(r)|^2/\rho(r)$ we obtain

$$\nu_{\text{xc}}(r) = \overline{\nu}(r) + [2\nu_{\text{xc},11}|\varphi_1(r)|^2 - \nu_{1,11}|\varphi_1(r)|^2 - \nu_{2,22}|\varphi_2(r)|^2]/\rho(r) - \frac{\Delta}{\delta}\left[2\left(1 - \frac{\delta}{\Delta}\right)\nu_{\text{xc},12} - \left(1 - \frac{\delta}{\Delta}\right)\nu_{1,12} + \left(1 + \frac{\delta}{\Delta}\right)\nu_{2,12}\right]\frac{\varphi_1(r)\varphi_2(r)}{\rho(r)}\,. \tag{7}$$

The third term in ν_{xc} is zero, the 1, 2 matrix elements (between φ_1 and φ_2) of ν_{xc}, ν_1 and ν_2 all being zero because of symmetry (the potentials are symmetric). The parameters Δ and δ we introduced in the orbital Green's functions therefore do not enter our solution for ν_{xc}, which is exact. The leading term, in fact the only surviving one, see below, is $\overline{\nu}(r)$, which arises from the δ-function part of the orbital Green's functions. It is easily verified that $\overline{\nu}(r)$ has exactly the desired behavior of being the potential due to a hole charge $-|a|^2$ when $r_1 \in \Omega_A$ and $-|b|^2$ when $r_1 \in \Omega_B$. Both ν_1 and ν_2 already have this behavior, and they contribute equally to $\overline{\nu}(r)$. We note that $\overline{\nu}(r)$ is the generalization of the Slater potential due to the Fermi hole, which can be written $\nu_S(r) = \sum_{i=1}^{N/2}\nu_i(r)2|\varphi_i(r)|^2/\rho(r)$ and which has been shown [15,17] to also arise from the δ-function part of the G_i. Since $\overline{\nu}(r)$ has proper Coulombic asymptotic behavior, the remaining term in the expression for ν_{xc} has to go to zero asymptotically, i.e., the free constant in ν_{xc} is fixed by the requirement $\nu_{\text{xc},11} = (\nu_{1,11} + \nu_{2,22})/2$, since for $R \to \infty$ both $|\varphi_1(r)|^2$ and $|\varphi_2(r)|^2$ tend to $\rho(r)/2 = (a^2 + b^2)/2$. (This is special for the present H_2 problem; in general such terms may lead to asymptotic divergence when φ is an unoccupied KS orbital.) The relation $\nu_{\text{xc},11} = (\nu_{1,11} + \nu_{2,22})/2$ generalizes the condition $\nu_{x,mm} = \nu_{m,mm}$ between the $\langle\varphi_m|\nu|\varphi_m\rangle$ matrix elements of ν_x and ν_m which Krieger *et al.* [15] derived for Coulombic asymptotic behavior of the exact-exchange potential, where φ_m is the highest occupied orbital.

The message of this paper is that it is possible to make an ansatz for an orbital dependent E_{xc} which fully

incorporates correlation effects. Employing an exchange-correlation hole built from occupied and unoccupied Kohn-Sham orbitals, as a natural extension of the exchange-only case, yields an exact Kohn-Sham solution for H_2 at $R \rightarrow \infty$, without symmetry breaking. We note that this type of exchange-correlation functional, which incorporates left-right correlation, is also capable of solving long-standing problems in DFT such as the improper dissociation behavior of two open shell atoms with different electronegativities. It also can help to prevent the huge overestimation in the (hyper)polarizabilities of systems such as long polyene and polyyne chains [18], as well as in (again) H_2 at long distance [19] (it has been indicated [18] that the failure of LDA and GGA for the polarizability in the polyene chains has partly the same physical origin of incorrect left-right correlation as their failure for H_2 polarizability at long distance). These applications will be discussed elsewhere.

In order to apply the functional proposed in general cases, two problems need to be solved. In the first place, an algorithm for the weights w_i for the orbitals in the hole amplitude $\varphi^{\text{hole}}(r_2 \mid r_1) = \sum_i [w_i \varphi_i^*(r_1)/\sqrt{\rho(r_1)}]\varphi_i(r_2)$ needs to be determined. In the context of one-matrix functional theory weights equal to the square roots of the NO occupation numbers, $\sqrt{n_i}$, have been advocated. Müller [20] already obtained weights $\sqrt{n_i}$ as an optimal choice by means of the Pauli principle, and in Refs. [6,13] it is demonstrated that $w_i = \sqrt{n_i}$ leads to a very accurate representation of actual holes, faithfully mimicking, apart from the left-right correlation hole in a chemical bond, the typical dynamical correlation holes in atoms: in-out polarization shape of the hole if the reference electron is close to a nucleus, angular structure at intermediate distances from the nucleus, and out-in polarization behavior at a large distance of the reference electron from the nucleus. Approximate optimization of the occupation numbers using the $\sqrt{n_i}$ weights along the entire dissociation coordinate of H_2 yielded good energies and occupation numbers close to the accurate NO occupation numbers from good wave functions. The $\sqrt{n_i}$ ansatz has also been applied in accurate atomic calculations (two-electron ions, C, Ne) [21] and has been further investigated and criticized [22–25]. For application of our (virtual) orbital dependent E_{xc} in the KS context in general situations we need an independent prescription for the w_i.

The second problem is that self-consistent calculations with the more elaborate orbital dependent forms of E_{xc} will require stable numerical solutions to the notoriously difficult problem of obtaining the inverse density response function χ_s^{-1}, for which recently good progress has been made [26,27]. Alternatively the techniques developed by Krieger *et al.* [15] may be employed, who in the exchange-only case elegantly solved the problem of inversion of χ_s, which arises physically from the arbitrary overall constant in the potential, by deriving the mentioned condition $\nu_{x,mm} = \nu_{m,mm}$ for proper Coulombic asymptotics of the potential. When unoccupied KS orbitals are involved asymptotic divergence of terms of the form $|\varphi_{j>N/2}|^2/\rho(r)$, as recently also identified in the case of a second order perturbation theory based on E_{xc} [28], has to be avoided.

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